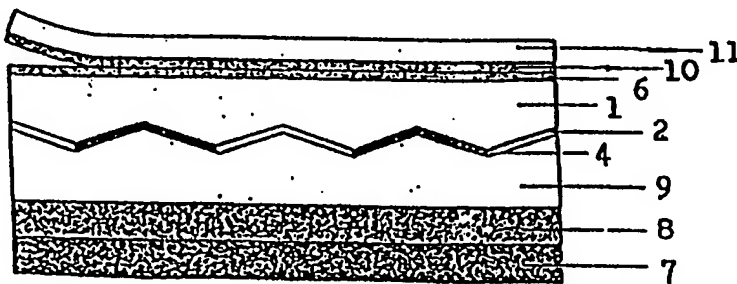




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/CZ99/00007 <b>(22) International Filing Date:</b> 11 March 1999 (11.03.99)  <b>(30) Priority Data:</b> PV 760-98                      13 March 1998 (13.03.98)                      CZ  <b>(71) Applicant (for all designated States except US):</b> ADIMEX, S.R.O. [CZ/CZ]; Úvoz 19, 602 00 Brno (CZ).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VLČEK, Miroslav [CZ/CZ]; Jana Zajíce 956, 530 12 Pardubice (CZ). SKLENÁŘ, Aleš [CZ/CZ]; Kudmova 376, 500 02 Hradec Králové (CZ).  <b>(74) Agent:</b> KUBÍČKOVÁ, Květoslava; České vysoké učení tech- nické, BIT ČVUT Patentové středisko, Zikova 4, 166 36 Praha 6 (CZ).		<b>(81) Designated States:</b> CA, JP, SK, US, Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> TRANSPARENT AND SEMITRANSSPARENT DIFFRACTIVE ELEMENTS, PARTICULARLY HOLOGRAMS AND THEIR MAKING PROCESS		
<b>(57) Abstract</b> <p>Transparent and semitransparent diffractive elements, particularly holograms with a diffractive pattern created at least in one of two following layers with different index of refraction: a transparent bearing layer (1) from polymer or copolymer having index of refraction <math>n &lt; 1,7</math>, and a holographic effect-enhancing, high refraction index layer (2) formed by chalcogenide based substances comprising at least one element from the group sulphur, selenium, tellurium, said layer (2) has <math>n &gt; 1,7</math> and its melting temperature is lower than 900 °C. The diffractive element can further contain a protective layer (6) and/or an adhesive layer (7) and/or a fragile layer (8) and/or an anchoring layer (9). The diffractive pattern is either formed in said bearing layer (1) and subsequently a high refraction index layer (2) (comprising one or more layers chalcogenide based substances of different composition, which can be deposited subsequently or simultaneously) is deposited on the said layer (1), or said layer (2) is firstly deposited onto said layer (1) and diffractive pattern is mechanically formed into this system.</p>		



Transparent and semitransparent diffractive elements, particularly holograms and their making process.

#### Background of the invention

5 This invention relates to a improvement of transparent and semitransparent diffractive elements and more particularly to a transparent and semitransparent type holograms and their making process. These diffractive elements are themselves transparent or semitransparent in visible (VIS) and/or near infrared (NIR) spectral region and yet are also endowed with the characteristics of a reflection type elements being observed under suitable  
10 angle. It means that reproduction in the transparent or semitransparent element of the present invention is effected only within specific reproduction angle range, while no hologram is recognised at other ordinary angles. This leads to the advantage that there is no visual obstruction of the article on which the diffractive element is laminated. Fig. 1 shows the basic constitution of the transparent or semitransparent diffractive element according to the present  
15 invention.

#### State of the art

Demand for holograms has grown not only as the way of the record of sound or information but as the elements used in such activities of human beings as advertisement, security  
20 sector, safety technique, protection of product originality, money counterfeit protection etc. It is well known that one of the following replication technologies is usually used for mass production of any diffractive elements in suitable polymer materials - hot embossing, injection moulding and casting.

Relief microstructure (master copy) is produced by one of the many high resolution fabrication  
25 technologies, the most commonly used being holographic exposure of suitable photosensitive material, including chalcogenides (US 3,825,317), direct writing with focused laser and e-beam, optical photolithography with subsequent wet or dry etching.

In most cases, a nickel shim or stamper is electroformed or replica is produced through  
30 casting into epoxy resin. These replicas are used for own mass production of copies into polymers using injection moulding (CD fabrication), casting (production of gratings for spectrophotometers) or hot embossing, for example into transparent foil (M.T. Gale: J. of Imaging Science and Technology 41 (3) (1997) 211).

Transparent polymeric materials such as polyethylene with index of refraction  $n = 1.5 - 1.54$ , polypropylene  $n = 1.49$ , polystyrene 1.6, polyvinyl chloride 1.52 - 1.55, polyester resin 1.52 -  
35 1.57 etc. (for more examples see US patent 4856857) or copolymers (for correction of index of refraction) can be used for transparent or semitransparent holograms and other diffractive elements production. Low refraction index value of these polymers or copolymers prepared from them determines their low reflectance ( $R$  about 4 %), hence the holographic effect of diffractive structure developed in layers of these polymers is insufficient (US patent  
40 4856857). Under the term "holographic effect" used in the following text we will understand

the phenomenon, that the hologram is very intensive in reflected light at suitable angle of observation. Low reflected intensity and thus the drawback of poor brightness of diffractive element recorded in the polymer layer is usually passed by forming a thin metallic film (generally Al) on the relief forming face of transparent polymeric layer (M. Miler: Holography -  
5 theoretical and experimental fundamentals and their application, SNTL, Prague 1974 (in Czech); M.T. Gale: J. of Imaging Science and Technology 41 (3) (1997) 211).

Strong improvement of brightness achieved at the cost of loss of the transparency is the main drawback of such technique. Transparency or at least semitransparency of diffractive element is required or desired in many applications (for example protective diffractive  
10 elements on banknotes, identity cards with photo etc.). Some technical applications of diffractive elements are directly conditioned by transparency or semitransparency of created element (for example microlense array for CCD cameras, polarising filters etc.).

It is further known that to preserve (or to decrease only partly) the transparency of diffractive element and at the same time to improve holographic effect of the hologram recorded in the  
15 polymeric layer (further called layer 1), it is necessary to cover layer 1 by other transparent layer (further called layer 2) of different material (further called holographic effect enhancing material) which has in general different index of refraction  $n$  (i.e. higher or lower) than material of the transparent layer 1 (US patent 4856857, US patent 5700550, US patent 5300764). The higher difference in index of refraction of polymeric bearing layer 1 and  
20 holographic effect-enhancing layer 2, the higher holographic effect can be achieved (US patent 4856857).

It is as well known that very thin layer (with thickness to the limit 20 nm) of suitable metal (e.g. Cr, Te, Ge) can be used as such layer 2 deposited on the transparent layer 1 in which a hologram has been hot-formed. Such very thin metallic layer being used, relatively high  
25 transparency is preserved. Relatively strong enhancing of holographic effect can be achieved when the index of refraction of deposited metallic layer is either significantly lower (e.g. Ag  $n = 0,8$ ; Cu  $n = 0,7$ ) or significantly higher (e.g. Cr  $n = 3,3$ , Mn  $n = 2,5$ , Te  $n = 4,9$ ) than index of refraction of transparent layer 1 ( $n$  about 1,5), (US patent 4856857). Such thin metallic layers are deposited at transparent, diffractive element bearing layer 1 by vacuum deposition  
30 technique. The drawback of the application of thin metallic layer as holographic effect enhancing material is relatively high melting point of these materials and therefore difficult evaporating of many of these metals. An additional drawback is high absorption coefficient of metals. Already slight deviations in the thickness of evaporated metal layer implicate significant deviations in the transmissivity of the system (layer 1 - bearing diffractive element  
35 + layer 2 - metal) and moreover upper limit of the permissible thickness is very low (it depends on the metal, but in general it must not exceed 20 nm (US patent 4856857)).

According to our measurements evaporation of either 10 nm thick Cr layer or 4 nm thick Ge layer on the polymeric layer decreases its transmissivity down to about 30 % (see Fig. 2).

In the present art, oxides of metals (e.g. ZnO, PbO, Fe<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, MgO etc.), halogenide  
40 materials (e.g. TiCl, CuBr, ClF<sub>3</sub>, ThF<sub>4</sub> etc.) eventually more complex dielectric materials (e.g.

KTa<sub>0.65</sub>Nb<sub>0.35</sub>O<sub>3</sub>, Bi<sub>4</sub>(GeO<sub>4</sub>)<sub>3</sub>, RbH<sub>2</sub>AsO<sub>4</sub> etc.) are used single or possibly in several layers deposited criss-cross as holographic effect enhancing layers (US patent 4856857). The drawback of the application of these materials is the fact that their index of refraction values are very close to the index of refraction of transparent polymeric layer 1 (e.g. index of refraction values are 1,5 for ThF<sub>4</sub>, 1,5 for SiO<sub>2</sub>, 1,6 for Al<sub>2</sub>O<sub>3</sub>, 1,6 for RbH<sub>2</sub>AsO<sub>4</sub> etc.) (US patent 486857). Accordingly an amplification of holographic effect is relatively low. Many of these materials require again relatively high temperature for their evaporation and not least some of them are quite expensive or hardly prepareable, what obstructs their mass application.

Further it is known, that binary chalcogenides of zinc and cadmium as well as compounds Sb<sub>2</sub>S<sub>3</sub> and PbTe (US patent 4856857), eventually multilayer systems of these chalcogenides with oxides or halides (US patent 5700550) or multilayer system ZnS and Na<sub>3</sub>AlF<sub>6</sub> (US patent 5300764) can be used as holographic effect enhancing. These materials are endowed with satisfactory index of refraction values (e.g. 3,0 for Sb<sub>2</sub>S<sub>3</sub>, 2,6 for ZnSe, 2,1 for ZnS). But short wavelength absorption edge of many of these materials (e.g. Sb<sub>2</sub>S<sub>3</sub>, CdSe, CdTe, ZnTe) lies within near IR region only and these materials are characterised by high values of absorption coefficient in VIS. Similarly with metal layer used as layer 2, only very thin layers of these materials can be used as holographic effect enhancing layer 2 to achieve at least semitransparency of final product. Transparency is again significantly influenced by thickness deviations. Additional significant drawback of these materials is their difficult vaporization (again similarity with metals) given by their high values of their melting points T<sub>0</sub> alfa - ZnS 1700 °C, beta - ZnS 1020 °C, ZnSe >1100 °C, ZnTe 1238 °C, CdS 1750 °C, CdSe > 1350 °C, CdTe 1121 °C, PbTe 917 °C) (Handbook of Chemistry and Physics 64th Edition 1983/84).

In the present art the process according to the scheme given in Fig. 3 is usually used in the mass production of transparent diffractive elements. Firstly a diffractive pattern is made in the layer 1, after it a thin dielectric or metallic layer is evaporated (perpendicularly or under specific incidence angle) a subsequently this evaporated layer is overlapped or laminated by another polymeric layer (M.T. Gale: Journal of Imaging Science and Technology 41 (3) (1997) 211). As above mentioned materials (metals, their oxides, halides, binary chalcogenides of Zn and Cd, Sb<sub>2</sub>S<sub>3</sub> and PbTe) are used as layer 2 in the production of diffractive elements by this way, the method has the same drawbacks, e.g. high melting temperatures determine difficult deposition, even small deviations in the thickness cause large deviations in the transmissivity, comparable index of refraction of many of these materials with index of refraction of polymeric layer 1, eventually full non transparency in VIS.

#### Subject matter of the invention

The present invention does away with the drawbacks of the present-day techniques of transparent and semitransparent diffractive elements production. The transparent or semitransparent diffractive element, particularly hologram of the present invention comprises a transparent polymeric (or co-polymeric) layer 1 with  $n < 1,7$  and a holographic effect

enhancing layer 2 (Fig. 1). The high refraction index layer 2 consists of matters based on chalcogenides containing at least one element from the group sulphur, selenium, tellurium with index of refraction higher than 1,7 and melting point lower than 900 °C. Chalcogenide based matters can be binary, ternary or even more complicated chalcogenides and/or chalcogenides and/or interchalcogenides systems containing beside S or Se or Te still as more electropositive element any of the following elements from I. to V. group of periodic table Cu, Ag, Au, Hg, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, N, P, As, Sb, Bi.

Chalcogenides based matters can contain further transient metal and/or at least one rare earth element, e.g. Pr, Eu, Dy.

- 10 Transparent or semitransparent diffractive element can further consists of other layers e.g. protective layer, adhesive layer, fragile layer, anchor layer. Protective layer protects layer 2 or layer 1 against environmental effect or against undesirable effect of consecutive exposure by UV light and improves resistivity of the final product. The layer can either be permanent part of the hologram or of the diffractive element or can be removable. Adhesive layer allows
- 15 unrepeatable or repeatable anchoring of the hologram or other diffractive element on protected article, printed document etc. The function of fragile layer is to adhere the upper layer and the lower layer and yet effect destruction of diffractive element during peeling for the purpose of forgery. Anchor layer is used to improve adhesivity of diffractive element to the base supporting sheet or to releasable sheet in the case of application as seal, sticker, label etc.

20 Transparent layer 1 can be inseparable part of some larger product, in such case the high refraction index layer 2 can be for example sprayed on the layer 1.

Procedure of transparent diffractive elements production consists of the formation of diffractive figure in a bearing layer 1 and subsequent deposition of high refraction index layer 2, which is formed with a chalcogenide based matters of different compositions. The deposition of different chalcogenide based matters can be consecutive or simultaneous.

- 25 Alternative way of transparent and semitransparent diffractive elements production is firstly to deposit high refraction index layer 2 on layer 1 and only after that to originate a required diffractive pattern into high refraction index layers at elevated temperature for example using hot embossing technique. If the depth of diffractive pattern is greater than the thickness of high refraction index layer 2 (very common situation), practically identical product (Fig. 1) is obtained as when the previous procedure is used. If the embossing depths are lower than thickness of high refraction index layer, the layer 1 operates as carrier of high refraction index layer 2 only.

- 30 High refraction index layer can be deposited on a previously coloured layer 1 and thus through the combination of their colours (colour of layer 2 depending on the composition and thickness used) a required colour effect of transparent or semitransparent diffractive element can be achieved.

- 35 High refraction index layer 2 can be deposited either at low pressure e.g. using vacuum evaporation, sputtering or chemical vapour deposition (CVD) technique or at normal pressure

as solution of chalcogenide based matters using e.g. spraying, painting or spin coating method.

The composition of high refraction index layer 2 formed with some chalcogenide based matters can be modified by exposure or annealing induced diffusion of metals and/or by halogens and/or oxygen, which are implanted into layer 2 by interaction of the layer 2 with halogen vapours or oxygen or by air hydrolysis.

Diffraction pattern formed in layer 1 and/or layer 2 can be further modified by exposure and/or by annealing and/or by selective etching.

Exposure with radiation of suitable wavelength and intensity (values depend on the particular composition of high refraction index layer (2), e-beam, ions, X-ray radiation etc. or annealing originates structural changes in high refraction index layer or it originates even changes in its chemical composition (e.g. diffusion of metal, which is in direct contact with high refraction index layer, hydrolysis, oxidation). Thereby a change of the value of index of refraction of layer 2 takes place (it usually increases) and thus the difference between values of index of refraction of bearing layer 1 and high refraction index layer 2 is modified. It results in a different optical perception of the product. A chemical reaction induced by exposure or by annealing, e.g. with surrounding atmosphere, can result in the transformation of chalcogenide material into fully different compound (e.g. oxide); the product of such reaction must again satisfy the condition, that its index of refraction is higher than 1.7.

Local exposure through the mask or holographic exposure or local annealing can produce a record of a further pattern, including hologram or other diffractive element into the high refraction index layer 2; the record can be either amplitude (based on different absorption coefficient of exposed and unexposed part of layer 2) or phase type based on either different values of index of refraction of exposed and unexposed parts of layer 2 or based on different thickness of exposed and unexposed parts of the layer 2 (different thickness can be achieved not only directly during exposure but also by consecutive etching of layer 2 by using well-known methods); even here can be used the phenomenon of local photoinduced diffusion, hydrolysis, oxidation etc. and the matter of high refraction index layer 2 can, in the place of local exposure or annealing change its chemical composition; resulting record in the high refraction index layer 2 can partly modify visual perception of the hologram and in addition it can be seen in view-through.

As index of refraction values of majority of chalcogenides exceed the value  $n = 2$ , application of chalcogenides layers as holographic effect enhancing layer 2 deposited on the transparent polymeric layers 1 with  $n < 1.7$  results generally in a significant visual perception. The transparency of final hologram or other diffractive element can be influenced through the thickness of layer 2.

Another important advantage of chalcogenide materials is the fact, that they can be synthesised in many systems in amorphous state and their glass forming regions are relatively wide. Being amorphous, these materials have not only very low scattering losses, but the possibility to prepare even nonstoichiometric compounds takes place. Gradual mutual

substitution of elements (not only S, Se and Te) in the composition of amorphous chalcogenides causes continuous changes in their index of refraction and reflectivity. Thus enhancement of holographic effect can be "tailored".

As a result of gradual mutual substitution of elements in the composition of amorphous chalcogenides arise gradual changes of their optical gap  $E_g^{opt}$  values (e.g.  $As_{40}S_{60}$   $E_g^{opt} = 2.37$  eV,  $As_{40}S_{40}Se_{20}$  2.07 eV,  $As_{40}Se_{60}$  1.8 eV) followed by gradual changes in the position of short wavelength absorption edge. Thus the colour (for given thickness) of layer 2 can be changed as well and transparent and semitransparent systems of different colours endowed with high holographic effect can be produced. So even colourless polymeric layers 1 can be used for production of transparent or semitransparent diffractive elements of required colour using one (or more) chalcogenide based layer of suitable composition as a layer 2. Thus composition and thickness of chalcogenide layer 2 influence significantly the transparency of final product (hologram) (Fig. 4) and reflectivity (Fig. 5) and thus intensity of holographic perception (it increases with the reflectivity of layer 2).

Amorphous chalcogenides are mainly as thin layers photosensitive to exposure with radiation of suitable intensity and wavelength (given by composition of the layer), e-beam, ions etc. This property enables us to provide an supplementary correction of index of refraction, reflectivity and transmissivity of high refraction index thin layer using exposure induced structural changes (Fig. 6), by exposure induced reaction of photosensitive chalcogenide layer with metal (e.g. Ag) (Fig. 6) or with gas ( $O_2$ , air humidity) induced transformation into different chemical substance, which must satisfy the condition that  $n > 1.7$ . Similar effect can be achieved by annealing.

If exposure or annealing are local only, procedures mentioned in the previous paragraph can result in the formation of an image (including holographic one) in the high refraction index layer, which can partly modify visual perception of the hologram and in addition it can be seen in view-through. Sectional views of structures developed using photoinduced structural changes and photoinduced metal diffusion are presented in Fig. 7 and 8.

Further advantage of above mentioned chalcogenides are their low melting temperatures (usually 100 - 300 °C). They can be therefore deposited by worldwide commonly used vacuum evaporation method. As the values of absorption coefficient in the region behind short wavelength absorption edge are low, even possible small deviation in the thickness influences much less the holographic effect enhancing than when thin metallic layers are used. Large areas of chalcogenide layers can be formed relatively easily using corresponding vacuum evaporation equipment. The thickness of the chalcogenide layer 2 can be adjusted by synchronising the evaporation rate with the feed speed of transparent bearing layer 1.

Further advantage of amorphous chalcogenides is the fact, that mass production of chalcogenides of many compositions exist worldwide and they are thus immediately commercially available at affordable price.

#### Brief description of the drawings

Fig. 1 Sectional view of the diffractive element of the present invention, 1 -transparent bearing polymeric layer with  $n_1 < 1,7$ , 2 - high refraction index chalcogenide based layer with  $n_2 > 1,7$

Fig. 2 Optical transmissivity T and reflectivity R of holograms produced by deposition of thin high diffractive index layer 2 formed by Cr or Ge on polyethylene layer 1 with hot embossed diffractive pattern

Fig. 3 Sectional views of sequence creation of transparent diffractive element based on the possibility of creation a diffractive pattern in bearing layer 1 and exploiting of the difference in index of refraction of layers number 1 and 2.

Fig. 4 Optical transmissivity of holograms produced by deposition of thin high diffractive index layer 2 formed by selected chalcogenide materials on polyethylene layer 1 with hot embossed diffractive pattern

Fig. 5 Reflectivity of holograms produced by deposition of thin high diffractive index layer 2 formed by selected chalcogenide materials on polyethylene layer 1 with hot embossed diffractive pattern

Fig. 6 Changes in optical transmissivity T of holograms created by photoexposure and by diffusion of Ag according to the techniques described in example 2 and 3.

Fig. 7 Sectional views of sequential steps of creation of transparent hologram or other diffractive element based on the possibility of creation of a diffractive pattern in bearing layer 1, exploiting the difference in index of refraction of layers number 1 and 2 and the photosensitivity of high refraction index chalcogenide layer 2.

Fig. 8. Sectional views of sequential steps of creation of transparent hologram or other diffractive element based on the possibility of creation a diffractive pattern in bearing layer 1, exploiting the difference in the index of refraction of layers number 1 and 2 and 5 ( $n_1, n_2, n_5$ ) and the photoinduced diffusion of metal 4 into chalcogenide layer 2 leading to origin metal doped high refraction index chalcogenide layer 5.

Fig. 9. Sectional view of possible final product - transparent hologram transfer sheet, which once being stuck on the protected article can not be peeled off without its destruction.

#### Examples of design

Following examples are given for better understanding of the present invention. Transparent polyethyleneterephthalate foil ( $n = 1,58$ ) with thickness  $50 \mu\text{m}$  or polycarbonate foil ( $n = 1,59$ ) with thickness  $60 \mu\text{m}$  were employed as layer 1 satisfying condition  $n < 1,7$ . Diffractive patterns were stamped into these layers using Ni shim and hot embossing method. Holograms and other diffractive elements, which were characterised by very low holographic effect, were further treated by some of the following processes given in examples 1 to 6. Application of thin chalcogenide layer as holographic effect enhancing, high refraction index layer 2 (Fig. 1) is the common vein in all these examples. The possibility to modify hologram or another diffractive element prepared by technique given in example 1 using well known phenomenon of photoinduced changes of the structure and properties of chalcogenides



used as high refraction index layer 2 is demonstrated in examples 2 - 4. Example 7 is demonstration of relief pattern production by stamping or pressing the pattern into system polymeric layer 1 - chalcogenide high refraction index layer 2 created in advance. All methods of fabrication of holograms or other diffractive elements fabrication given in Examples 1 - 7 can be used for production of more complicated final products, sectional view of one of them is given in Fig. 9. Example of one simpler application of transparent holograms of the present invention is given in the Example 8.

#### Example 1

Thin layers ( $d = 10 - 500 \text{ nm}$ ) of  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  composition ( $n = 2,25$ ) were deposited by vacuum evaporation method (deposition rate  $1 \text{ nm/sec}$ , pressure  $5 \cdot 10^{-4} \text{ Pa}$ ) on bearing layer 1 from the side of relief pattern fabricated beforehand in layer 1. In all cases sufficient holographic effect has been achieved as a result of a greater reflected light intensity. Relatively high transparency of prepared system has been preserved. Reflectivity (Fig. 5 curves 1,2) and transmissivity (Fig. 4 curves 2, 5 and Fig. 6 curve for  $d = 30 \text{ nm}$ ) of obtained structures depend on the thickness of deposited high refraction index layer 2. Thicker layers (of the order hundreds nanometers) being used, spectral dependence of the optical transmissivity and reflectivity was influenced strongly by interference phenomena, as wavelength of VIS and NIR radiation is comparable with thickness of high refraction index layer 2.

Similar results were obtained when other chalcogenide materials, e.g.  $\text{Ge}_{20}\text{Sb}_{25}\text{Se}_{55}$  ( $n = 3,11$ ),  $\text{As}_{50}\text{Ge}_{20}\text{Se}_{30}$  ( $n = 2,95$ ),  $(\text{As}_{0,33}\text{S}_{0,67})_{90}\text{Te}_{10}$  ( $n = 2,3$ ) were applied as layer 2. Results of application of further chalcogenide based systems  $\text{Ag}_8\text{As}_{36,9}\text{Se}_{55,1}$ ,  $\text{Ge}_{20}\text{Sb}_{10}\text{S}_{70}$ ,  $\text{As}_{40}\text{S}_{40}\text{Se}_{20}$ ,  $\text{As}_{20}\text{Se}_{40}\text{Te}_{40}$  as layers 2 satisfying condition  $n > 1,7$  are given in Fig. 4 - 6. Similar results were achieved when other binary (e.g.  $\text{Se}_{90}\text{Te}_{10}$ ,  $\text{Ge}_{33}\text{S}_{67}$ ), ternary (e.g.  $(\text{As}_{0,33}\text{S}_{0,67})_{95}\text{I}_5$ ) or even more complicated (e.g.  $\text{As}_{40}\text{S}_{40}\text{Se}_{10}\text{Ge}_{10}$ ) chalcogenides were applied as layer 2. Thin layers of more complicated systems can be prepared either by vacuum evaporation of bulk samples of the same composition or by simultaneous evaporation of more simple chalcogenides from two boats (e.g.  $\text{As}_{40}\text{S}_{60}$ ,  $\text{Ge}_{33}\text{S}_{67}$ ,  $\text{As}_{40}\text{Se}_{60}$  etc.). Enhancement of holographic effect has been achieved as well when chalcogenide layers were deposited sequentially, e.g. two different holographic effect enhancing layers were deposited sequentially. Thin layers of some chalcogenides (mainly of sulphides, e.g.  $\text{Ge}_{33}\text{S}_{67}$ ) are relatively unstable in the air and can be hydrolysed, thus oxygen can be built in their structure. Even thus hydrolysed layers operate as holographic effect enhancing layers

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#### Example 2

Thin layer  $\text{As}_{42}\text{S}_{58}$  with thickness  $100 \text{ nm}$  was deposited by technique presented in example 1 on the carrying layer 1. Thus a significant holographic enhancing effect was achieved and the hologram recorded in carrying layer 1 was clearly visible under suitable angle of observation. The system prepared by this way was modified using above described phenomenon of

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photoinduced structural change in high refraction index layer 2 (where exposed, the layer is transformed into a state marked as number 3 in Fig. 7). Exposition of the system from the index of refraction layer 2 side by UV lamp ( $I = 18 \text{ mW/cm}^2$ ) for 300 sec caused a changed optical transmissivity of the system (Fig. 6) accompanied with increase of index of refraction value for about 0,1 and thus holographic effect was enhanced as well. Local exposure through the mask caused only local changes in the transmissivity and index of refraction (layer 3 in Fig.7) and thus a negative picture (exposed parts are less transparent) of used mask was developed in  $\text{As}_{42}\text{S}_{58}$  layer, which can be seen in view-through and modifies the optical perception of the hologram recorded in the layer 1 when this is observed in reflection.

Similar results were achieved when after deposition of  $\text{As}_{42}\text{S}_{58}$  layer, still before its exposure, the system layer 1 - layer 2 was treated in iodine vapours, what transformed composition of layer 2 into As-S-I (real composition depends on the temperature and concentration of  $\text{I}_2$ ). Even without subsequent exposure chalcogenide As-S-I layer had an enhanced holographic effect.

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#### Example 3

Thin  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  layer with thickness 30 nm and subsequently 10 nm thin Ag layer (layer 4 in Fig. 8) were deposited by technique presented in example 1 on carrying layer 1. Consecutive 300 sec exposure with Xe lamp ( $I = 20 \text{ mW/cm}^2$ ) induced diffusion of Ag into  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  layer, which was local only when exposition was provided through the mask (new composition layer Ag- $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$ , marked as layer 5 in Fig 8). New Ag- $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  layer has generally a higher value of index of refraction than  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  layer, final value depending on the amount of diffused silver. Excessive, unreacted Ag was striped by dipping in diluted  $\text{HNO}_3$  (1:1) and thus the picture of the mask was recorded into original layer 2. This picture can be seen in view-through and modifies optical perception of the hologram recorded in the layer 1 when this is observed in reflection.

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#### Example 4

Final product fabricated in example 3 was further immersed in 0,02 mol/l KOH solvent, in which only high refraction index layer 2 is partly soluble. Layer 5 is resistant against this solvent. Thus a relief picture is formed in chalcogenide layer which can be seen in view-through and which again modifies optical perception of the hologram recorded in the layer 1 when this is observed in reflection.

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#### Example 5

Thin layer ( $d = 40 \text{ nm}$ ) of  $\text{Ge}_{24,6}\text{Ga}_{10,2}\text{S}_{64,8}\text{Pr}_{0,35}$  was deposited by vacuum evaporation method (deposition rate  $1 \text{ nm/sec}$ , pressure  $5 \cdot 10^{-4} \text{ Pa}$ ) on the bearing layer 1 from the side of relief pattern fabricated beforehand in layer 1. Application of these materials as a high refraction index layer resulted again in the enhancement of the holographic effect, e.g. hologram recorded in carrying layer 1 was well seen when observed under specific angle.

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#### Example 6

Thin  $\text{As}_{40}\text{S}_{60}$  layer was deposited using spin coating method at normal pressure on the polycarbonate bearing layer 1 from the side of relief pattern fabricated beforehand in layer 1.

5 Starting solution  $\text{As}_{40}\text{S}_{60}$  in n-propylamine was used in concentration 0,8 mol/l. Thicknesses of prepared layers were in range 0,5 - 2  $\mu\text{m}$ . Deposition of  $\text{As}_{40}\text{S}_{60}$  layer again led to partial improvement of optical perception of the hologram recorded in the layer 1 when this was observed in reflection.

10 Similar results were achieved when solutions of  $\text{As}_{33}\text{S}_{67}$  or  $\text{As}_{40}\text{S}_{60}$  in n-propylamine or triethylamine were used either for spin coating deposition or these solvents were only painted on bearing layer 1.

#### Example 7

15 Thin  $\text{As}_{35}\text{S}_{65}$  layer ( $d = 30 \text{ nm}$ ) was deposited by vacuum evaporation method on polycarbonate bearing layer 1. Relief structure was stamped into this bilayer from the side of high refraction index layer 2 by hot embossing at temperature about 150 °C. After a couple of minutes at this temperature, the whole system was cooled down and only after that thrust released. The product had similar properties as when  $\text{As}_{35}\text{S}_{65}$  layer of identical thickness was used to prepare hologram by the technique described in Example 1. An identical result was  
20 achieved when  $\text{As}_{35}\text{S}_{65}$  layer was deposited on layer 1 by CVD method.

#### Example 8

Thin layers ( $d = 20 \text{ nm}$ ) of  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  composition ( $n = 2,25$ ) was deposited by vacuum evaporation method (deposition rate 1 nm/sec, pressure  $5 \cdot 10^{-4} \text{ Pa}$ ) on bearing layer 1 from  
25 the side of relief pattern beforehand fabricated in layer 1. Obtained hologram was set on document with text and photo (which had to be protected by applied transparent hologram) and sealed with the document into 175  $\mu\text{m}$  thick polyester foil provided with fusible paste. With regard to high transparency of the hologram (45% - 85 % in spectral region 400 - 750 nm, see Fig. 4 curve 5) were both, text and photo, very well readable and at the same time  
30 with regard to high reflection (24-15%, Fig. 5 curve 2) the hologram formed in the bearing layer 1 was very well seen being observed under specific angle.

Similar results (with different level of transparency and holographic effectiveness depending on the composition and thickness of layer 2) were obtained when other holograms endowed with enhanced holographic effect caused by application of chalcogenide thin layer 2 prepared  
35 by methods presented in examples 1 - 7 were used as counterfeit protecting elements.

Example of one diffractive structure which can be prepared according to the present invention is given in Fig. 3 (including processing) and an example of one possible multilayer hologram is presented in Fig. 9, where 6 stands for protecting layer which protects a high refraction  
40 index layer 2 or bearing layer 1 against environmental effect or against undesirable effect of

consecutive exposure by UV light and improves resistivity of the final product, 7 stands for adhesive layer which enables either unrepeatable or repeatable anchoring of the hologram or other diffractive element on the protected article, 8 stands for fragile layer which ensures good adherence of two layers to each other and which depreciates itself during any attempt  
5 to peel off and thus causes irreversible deformation and destruction of the diffractive element, 9 stands for the anchor layer, which is usually used to improve adherence of adhesive layer 7 to high refraction index layer 2 or to the bearing layer 1, 10 stands for adhesive layer providing clutching of hologram to the carrier 11 before its own application.

10 Industrial exploitation

The present invention is applicable for fabrication of transparent and semitransparent diffractive elements and more particularly to a transparent and semitransparent type holograms. Besides of technical applications (e.g. record of picture or information) these products can be used in such activities of human beings as advertisement, security sector,  
15 safety technique, protection of product originality, money counterfeit protection etc.

## PATENT CLAIMS

1. Transparent and semitransparent diffractive elements, particularly holograms, consisting at least of two layers with a different index of refraction, whereof a first bearing layer (1) is a transparent polymer or copolymer having index of refraction lower than 1,7 and on said first carrying layer is deposited a second holographic effect enhancing high refraction index layer (2), characterized in that in at least one layer a diffraction pattern is shaped, and the high refraction index layer (2) constituted by substances based on chalcogenides comprising at least one of the elements from the group sulphur, selenium, tellurium, has an index of refraction higher than 1,7 and a melting temperature lower than 900 °C, the said chalcogenide based substances being selected from the group of binary, ternary and even more complex chalcogenide and/or chalcohalogenide systems, containing, in addition to S or Se or Te, as a more electropositive element some of the elements of the I. to V. group periodical table of the elements Cu, Ag, Au, Hg, B, Al, Ga, In, Tl, Si, Ge, Sn, Pb, N, P, As, Sb, Bi.
2. Transparent and semitransparent diffractive elements according to claim 1, characterized in that the chalcogenide based substances also contain at least one transient metal and/or at least one element from the rare earth element group.
3. Transparent and semitransparent diffractive element according to claims 1 and 2, characterized in that it also consists of a protecting layer (6) and/or an adhesive layer (7) and/or a fragile layer (8) and/or anchoring layer (9).
4. A production process of transparent and semitransparent diffractive elements according to claims 1 to 3, characterized in that a diffractive pattern is formed in the said layer (1) and subsequently on said bearing layer (1) the said high refraction index layer (2) is deposited, consisting of one or several layers of chalcogenide based substances of different composition, while the deposition of various chalcogenide based substances can be performed subsequently or simultaneously.
5. A production process according to claims 1 to 2, characterized in that the said high refraction index layer (2) is first deposited on the transparent bearing layer (1) and only after that a diffractive pattern is mechanically formed in said high refraction index layer (2).
6. A production process according to claims 4 and 5, characterized in that the high refraction index layer (2) is deposited on said bearing layer (1) coloured in advance.
7. A production process according to claims 4, 5 and 6, characterized in that the high refraction index layer (2) is deposited under low pressure, e.g. by vacuum evaporation, sputtering or chemical vapour deposition (CVD) technique.
8. A production process according to claims 4, 5 and 6, characterized in that the high refraction index layer (2) is deposited under atmospheric pressure, e.g. by spraying, painting or spin coating method.
9. A production process according to claims 4 to 8, characterized in that the high refraction index layer (2) consisting of chalcogenide based substances is modified with metal using metal diffusion induced by exposure or annealing and/or with a halogen or oxygen implanted

into the high refraction index layer (2) composed of chalcogenide based substances by its interaction with halogene vapours or interaction with oxygen or through air hydrolysis.

10. A production process according to claims 4 to 9, characterized in that the diffractive pattern formed in said bearing layer (1) and/or in said high refraction index layer (2) is
- 5 modified in addition by exposure to radiation and/or annealing and/or selective etching.

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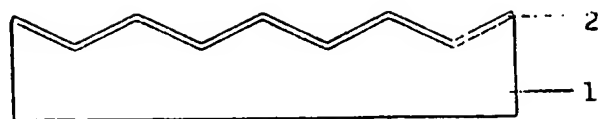


Fig. 1

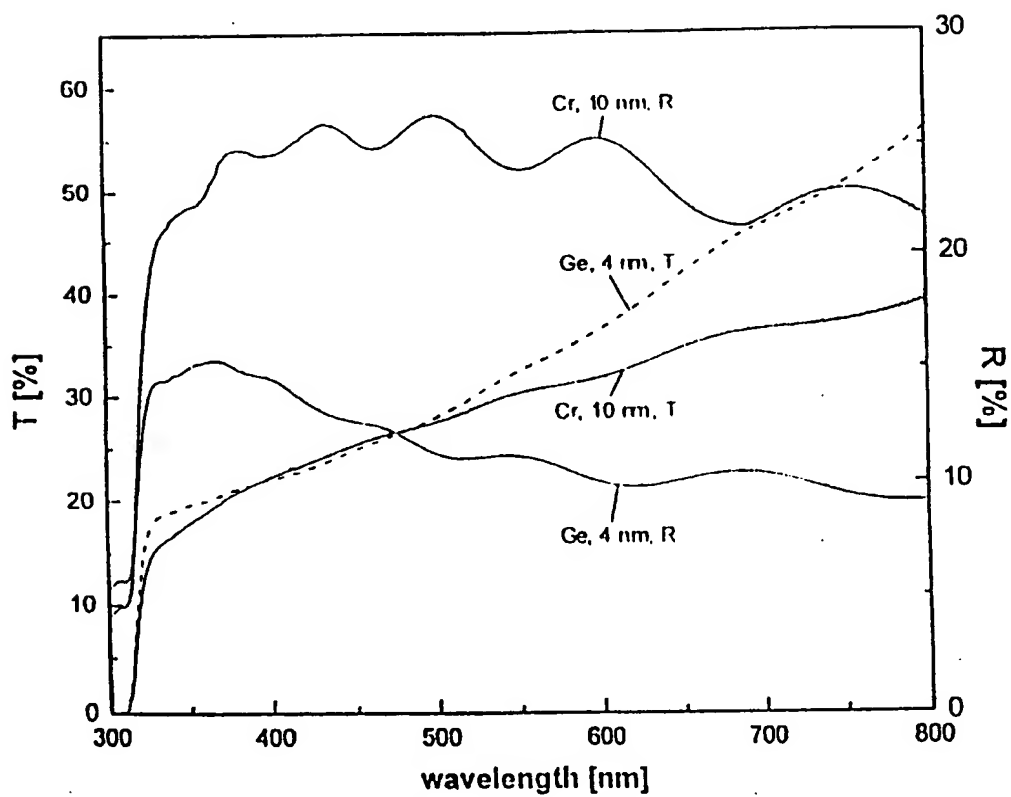


Fig. 2

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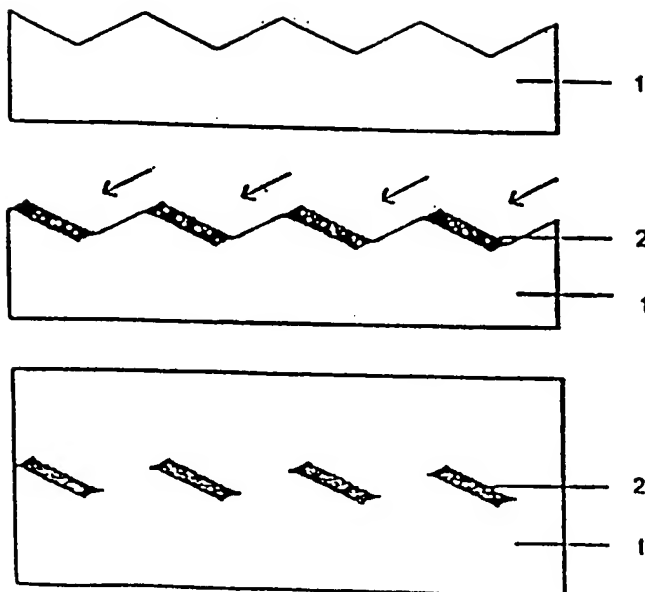


Fig. 3

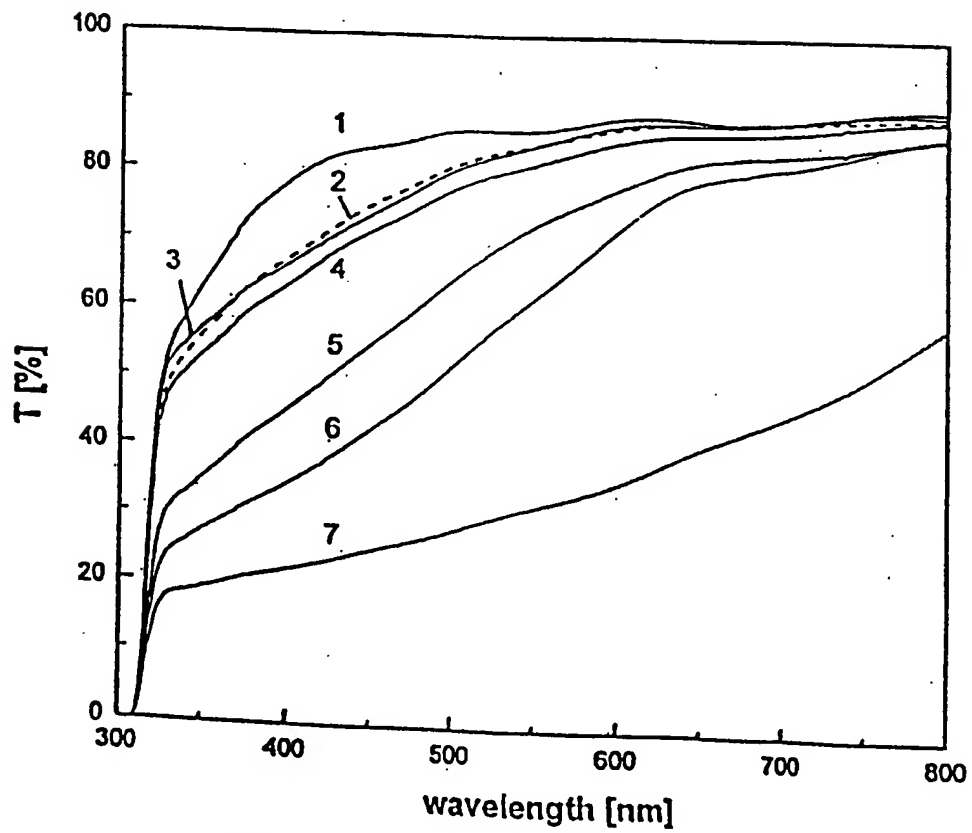


Fig. 4

1 -  $\text{Ge}_{20}\text{Bi}_{10}\text{S}_{70}$ , 15 nm  
 2 -  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$ , 10 nm  
 3 -  $\text{Ge}_{15}\text{Sb}_{25}\text{Se}_{60}$ , 10 nm  
 4 -  $\text{As}_2\text{Se}_3$ , 10 nm

5 -  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$ , 20 nm  
 6 -  $\text{Ag}_6\text{As}_{36.9}\text{Se}_{55.1}$ , 20 nm  
 7 -  $\text{Cu}_{35}\text{Te}_{30}\text{Se}_{35}$ , 15 nm



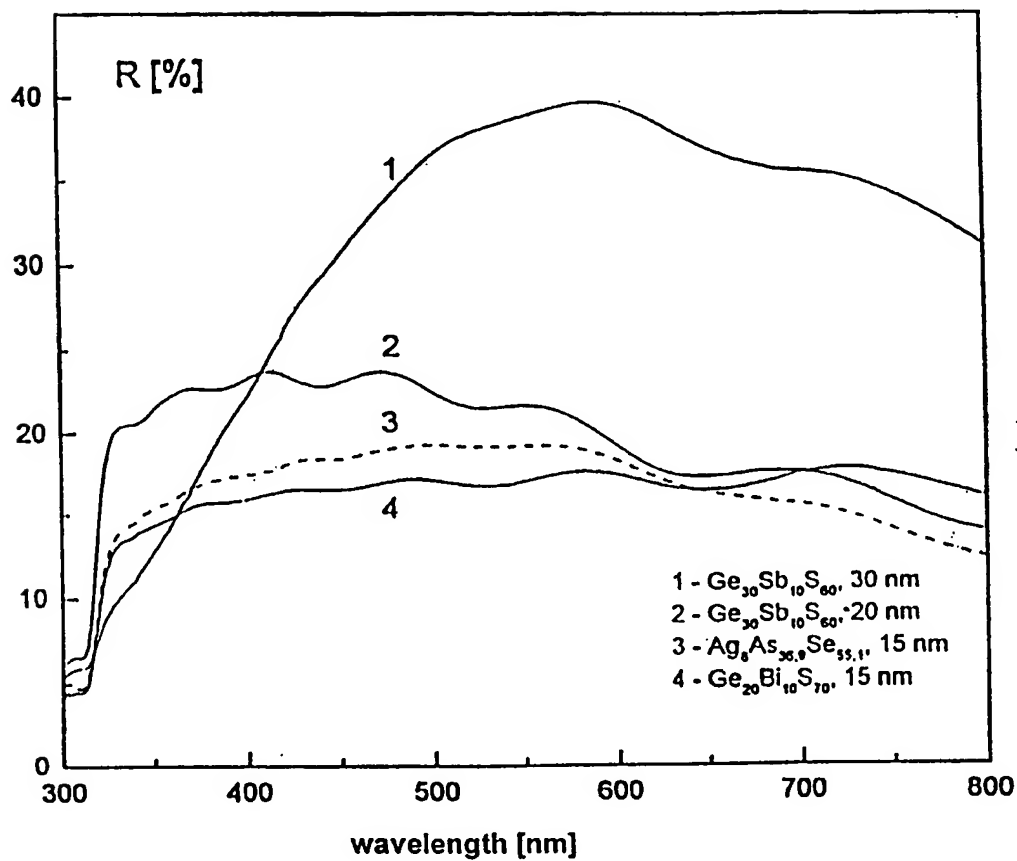


Fig. 5

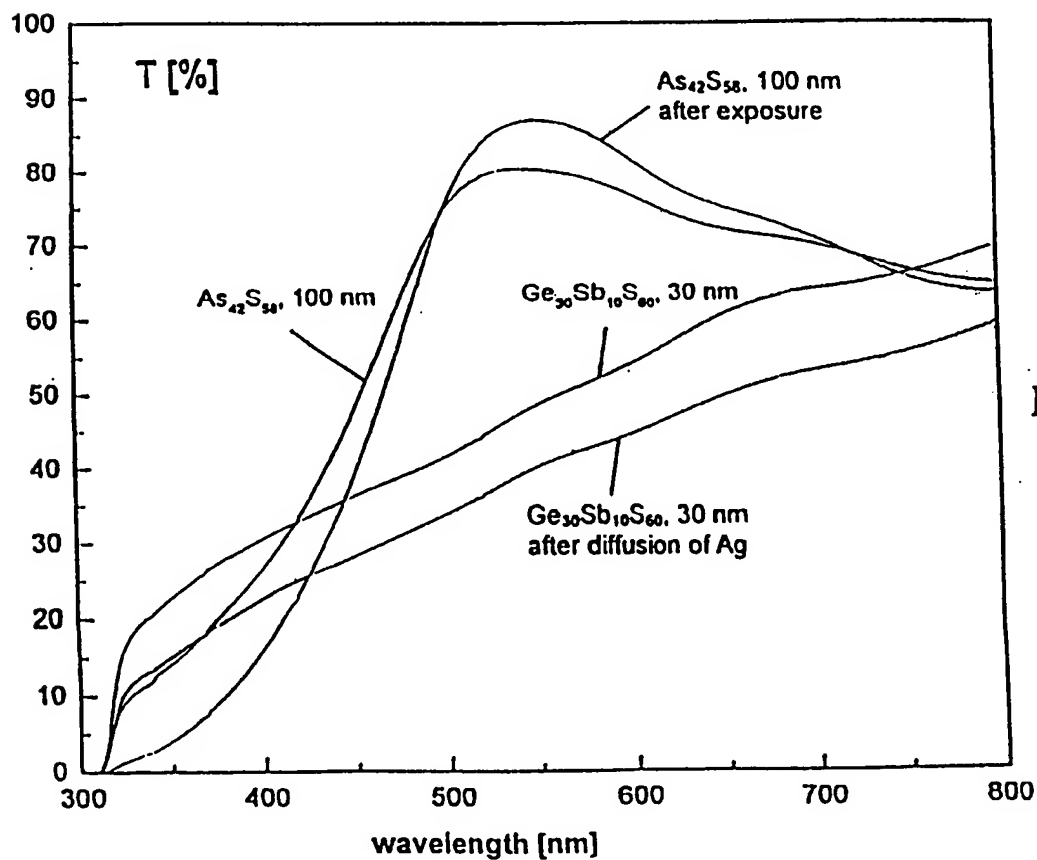


Fig. 6

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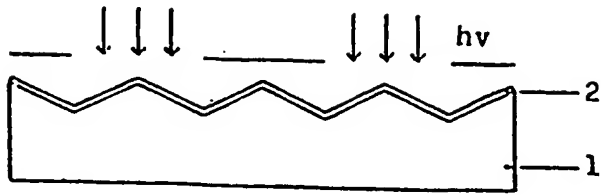


Fig. 7

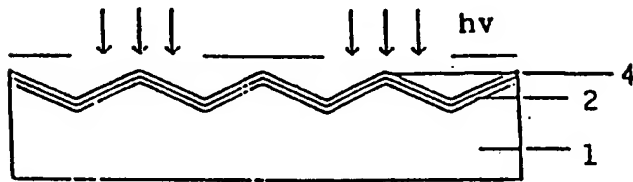
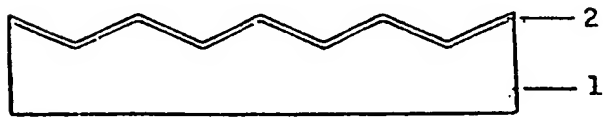
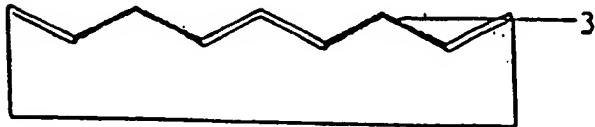


Fig. 8

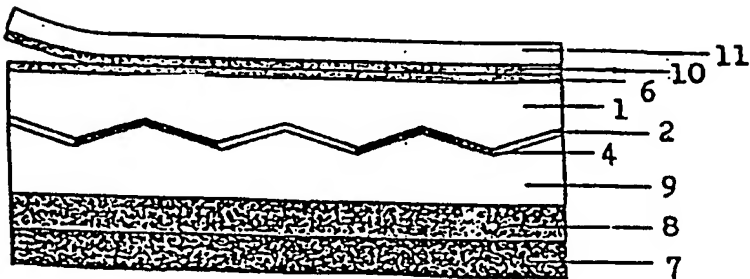
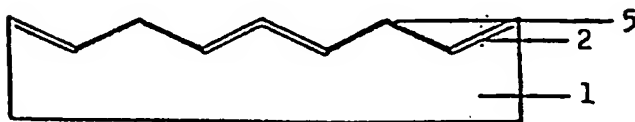


Fig. 9

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/CZ 99/00007

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G03H1/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 856 857 A (TAKEUCHI SATOSHI ET AL) 15 August 1989 cited in the application see column 2, line 30 - line 35 see column 4, line 35 - column 5, line 7 see column 6, line 65 - column 8, line 35 see column 9, line 52 - line 61 see column 12, line 22 - line 42 see table 1 ---	1,3,7
A	US 3 825 317 A (INOUE E ET AL) 23 July 1974 cited in the application see column 3, line 19 - column 4, line 25 see column 17, line 43 - column 18, line 40 see claims 1,3 --- -/--	1,2,7-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

24 June 1999

Date of mailing of the international search report

01/07/1999

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# INTERNATIONAL SEARCH REPORT

International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	<p>US 5 496 072 A (ANDO JITSUHIKO ET AL)</p> <p>5 March 1996</p> <p>see column 4, line 43 - line 49</p> <p>see column 10, line 56 - column 11, line 18</p> <p>see figures 1,8,10</p> <p>-----</p>	1,3

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